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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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	Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: CENTRIFUGALLY ATOMIZED ZINC ALLOY POWDER FOR ALKALINE BATTERIES

(57) Abstract

This invention relates to centrifugal atomized zinc alloy powders for alkaline batteries consisting of (a) 0.005–2 % by weight of indium, and 0.005–0.2 % by weight of either one of Al and Bi, or (b) 0.005–2 % by weight of indium, and 0.005–0.2 % by weight of Bi, and 0.001–0.5 % of either one or both of Al and Ca, or (c) 0.005–2 % by weight of either one or both of Bi and Al, and 0–0.5 % by weight of Pb, the remainder being zinc. The powder is obtained by centrifugal atomisation in a protective atmosphere, where the oxygen content is less than 4 % by volume. The resistance to corrosion in the electrolyte of the battery, especially after partial discharge, is markedly better than when the same alloys are prepared by the traditional production process. The capacity of batteries containing these powders is very good.

INTERNATIONAL SEARCH REPORT

Inte nal Application No
PCT/EP 00/00932

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M4/42 C22C1/04 B22F9/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M C22C B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 254 (E-72), 13 June 1989 (1989-06-13) & JP 01 052379 A (MITSUI MINING & SMELTING CO LTD; OTHERS: 01), 28 February 1989 (1989-02-28) abstract --- PATENT ABSTRACTS OF JAPAN vol. 010, no. 228 (E-426), 8 August 1986 (1986-08-08) -& JP 61 064074 A (TOSHIBA BATTERY CO LTD), 2 April 1986 (1986-04-02) abstract ---	1-10
X	---	1-10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *8* document member of the same patent family

Date of the actual completion of the international search

9 June 2000

Date of mailing of the international search report

19/06/2000

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

Int'l. Application No.
PCT/EP 00/00932

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 008, no. 069 (M-286), 31 March 1984 (1984-03-31) & JP 58 217608 A (TOYOU KINZOKUKO KK; OTHERS: 01), 17 December 1983 (1983-12-17) abstract ---	1-10
A	WO 94 19502 A (UNION MINIERE SA ;STRAUVEN IVAN A J (BE); MEEUS MARCEL L (BE)) 1 September 1994 (1994-09-01) cited in the application * whole document * page 3, line 14 - line 31 examples claims ---	1-10
A	US 5 082 622 A (STRAUVEN YVAN ET AL) 21 January 1992 (1992-01-21) cited in the application column 1, line 49 -column 2, line 24; table claims ---	1-10
A	WO 96 06196 A (UNION MINIERE SA ;STRAUVEN IVAN A J (BE); MEEUS MARCEL L (BE)) 29 February 1996 (1996-02-29) page 3, line 1 - line 18 examples claims ---	1-10
A	WO 96 07765 A (UNION MINIERE SA ;STRAUVEN IVAN A J (BE); MEEUS MARCEL L (BE)) 14 March 1996 (1996-03-14) page 3, line 14 - line 29 examples claims ---	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/00932

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
JP 01052379	A	28-02-1989	NONE		
JP 61064074	A	02-04-1986	JP 1687835 C	11-08-1992	
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			AU 3383895 A	14-03-1996	
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			ES 2126929 T	01-04-1999	
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WO 9607765	A	14-03-1996	BE 1008715 A	02-07-1996	
			AU 3472695 A	27-03-1996	

28-10-2000

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Table 3: Discharge time of batteries prepared with centrifugally atomised vs.
gas jet atomised powders

Ex. No.	Alloy powder additives (ppm)					(***)	O_2 % by Volume	Discharge time (%)
	In	Bi	Ca	Al	Pb			
(29)	160	230	-	-	46	C	2.35	102
(30)	160	230	-	-	46	C	0.6	90
(31)	160	230	-	-	46	G	2.35	87
(32)	160	230	-	-	46	G	0.6	61

(***) : 'C': centrifugal atomized powder; 'G': powder preparation by gas jet

5 atomisation

The results of Experiment 3 are the following:

- both discharge times for centrifugally atomised powders are within the claimed range of 90-110% of the discharge time of the standard powder. 2.35%
- 10 O_2 yields a better capacity than 0.6% O_2 .
 - both discharge times for the gas atomised powder are significantly lower than the discharge times of powders atomised centrifugally in gas with the same composition of the powder and of the protective atmosphere, and are less than 90%.

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In Table 4 additional results for powders prepared by centrifugal atomisation according to the invention are given. They have been prepared and tested following the procedure of Experiment 1.

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Table 4: Volume expansion of different centrifugally atomised powders

Ex. No.	Alloy powder additives (ppm)					O ₂ % by Volume	Volume expansion (%)
	In	Bi	Ca	Al	Pb		
(33)	250	250	150	-	-	0.6	3.3
(34)	500	110	-	35	-	0.6	1.9
(35)	500	110	-	35	-	1.35	2.5
(36)	500	110	-	35	-	1.6	2.1
(37)	500	110	-	35	-	2.1	6.7
(38)	500	110	-	35	-	2.6	7.6
(39)	150	230	-	-	-	1.6	5.5
(40)	200	100	-	100	-	1.6	4.0
(41)	200	100	-	100	-	2.6	2.9
(42)	150	230	-	-	-	0	5.6
(43)	150	230	-	-	-	2	7.3
(44)	200	100	-	100	40	2	2.7
(45)	150	230	-	-	38	2.45	6.7
(46)	150	230	-	-	55	0.25	5.0
(47)	200	100	-	100	40	3.5	3.7

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

KNOCKAERT, Guy
N.V. UNION MINIERE S.A.
Patent Department
Kasteelstraat 7
B-2250 Olen
BELGIQUE

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing (day/month/year)	24.11.2000
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Applicant's or agent's file reference 211	IMPORTANT NOTIFICATION	
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International application No. PCT/EP00/00932	International filing date (day/month/year) 03/02/2000	Priority date (day/month/year) 09/02/1999
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Applicant N.V. UNION MINIERE S.A. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/	Authorized officer
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European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Krage, D
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Tel. +49 89 2399-7530



PATENT COOPERATION TREATY**PCT****INTERNATIONAL PRELIMINARY EXAMINATION REPORT**

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 211	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP00/00932	International filing date (day/month/year) 03/02/2000	Priority date (day/month/year) 09/02/1999
International Patent Classification (IPC) or national classification and IPC H01M4/42		
Applicant N.V. UNION MINIERE S.A. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

- I Basis of the report
- II Priority
- III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV Lack of unity of invention
- V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI Certain documents cited
- VII Certain defects in the international application
- VIII Certain observations on the international application

Date of submission of the demand 09/08/2000	Date of completion of this report 24.11.2000
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523856 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Mizera, E Telephone No. +49 89 2399 8580

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP00/00932

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).;*):

Description, pages:

1-7 as originally filed

8,9 as received on 28/10/2000 with letter of 25/10/2000

Claims, No.:

1-10 as originally filed

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

**INTERNATIONAL-PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP00/00932

5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees the applicant has:

- restricted the claims.
- paid additional fees.
- paid additional fees under protest.
- neither restricted nor paid additional fees.

2. This Authority found that the requirement of unity of invention is not complied and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

- complied with.
- not complied with for the following reasons:
see separate sheet

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

- all parts.
- the parts relating to claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, Inventive step or Industrial applicability; citations and explanations supporting such statement**1. Statement**

Novelty (N)	Yes:	Claims	7-10
	No:	Claims	1-6

Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-10

Industrial applicability (IA)	Yes:	Claims	1-10
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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP00/00932

No: Claims

2. Citations and explanations
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP00/00932

The following documents are cited:

D1: PATENT ABSTRACTS OF JAPAN vol. 013, no. 254 (E-772), 13 June 1989 (1989-06-13) & JP 01 052379 A (MITSUI MINING & SMELTING CO LTD; OTHERS: 01), 28 February 1989 (1989-02-28)

D2: WO 94 19502 A (UNION MINIERE SA ;STRAUVEN IVAN A J (BE); MEEUS MARCEL L (BE)) 1 September 1994 (1994-09-01) cited in the application

AS TO BOX IV:

1. Claim 1 comprises three alternatives which are linked by the presence of Zn and the amount of Bi as common feature. Such alloys, however, are already known from the prior art (see D2, claim 1, example 1 and p.1, l.19).
2. The process feature contained in this claim not being suitable to establish novelty of a product claim (see Box V), the alternatives contained in claim 1 lack unity 'a posteriori'.
3. Anyway possibly patentable subject matter only seems to be contained in a product claim in which the product is defined in terms of the essential product features. As claim 1 clearly does not meet the requirements of the PCT, no invitation to pay additional fees had to be sent.

AS TO BOX V:

1. Claim 1 differs from the disclosure of D2 only by features concerning the process used for the fabrication of the claimed powder (i.e. the powder prepared in D2 is obtained by atomizing the molten alloy in a jet of compressed air).
2. According to the applicant, the powder of the invention exhibits a better corrosion resistance, which is claimed to be derivable from the gassing tests shown in Table 1.
3. This argumentation, however, is not convincing. Alloy powders 11, 12 and 17, 18 exhibit a gassing behaviour that is at least as good as the gassing of the claimed

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP00/00932

electrodes, although the experiments with these electrodes have been conducted in air.

4. Moreover product-by process claims are only acceptable in exceptional cases. In the present case it would have been easily possible to further characterize the claimed powder in terms of conventional parameters, such as particle size and oxygen content. Such a definition would have been absolutely necessary, as these parameters depend largely upon process parameters such as temperature, rotation speed and exact composition of the atmosphere used. In the lack of such parameters, the claimed product is not sufficiently defined in order to allow a reasonable comparison with the prior art. Novelty of claims 1-6 thus cannot be acknowledged (Art.33(2) PCT).
5. D1 deals with a problem that is also 'at the heart of the present invention', i.e. the reduction of hydrogen gas evolution in spite of a low amalgamation. D1 teaches also an atomization of Zn alloy powder at an oxygen content that is controlled to 4vol% or less. A skilled man dealing with gas atomization methods for the preparation of Zn alloy powder must be expected to know this document in this fairly limited technical area. He immediately gets the incentive to try the atmosphere used also according to claim1. Consequently the combination of the teachings of D1 and D2 is obvious. Claims 7-10, directed to methods for the production of the powder, thus lack an inventive step under Art.33(3)PCT.